

PORTLAND HARBOR RI/FS  
REMEDIAL INVESTIGATION REPORT

**APPENDIX D3.3**  
**PATTERNS AND TRENDS OF PCBs, PCDD/Fs, DDX,  
AND PAHS IN SURFACE WATER**

June 12, 2015

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## APPENDIX D3.3 PATTERNS AND TRENDS OF PCBS, PCDD/FS, DDX, AND PAHS IN SURFACE WATER

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### D3.3.1 Introduction

Section 5.4 of the remedial investigation (RI) report presents the extent of concentrations of the 13 indicator contaminants in surface water. This appendix provides additional details on the nature of the four grouped indicator contaminants, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), DDX<sup>1</sup>, and polycyclic aromatic hydrocarbons (PAHs), in surface water by examining the patterns in the occurrence of the constituent contaminants that make up these compound groups. The detail provided here helps inform discussion of the conceptual site model (Section 10) and identification of potential sources and contaminant transport.

### D3.3.2 Patterns and Trends of PCBs in Surface Water

The patterns and trends of PCB homologs in surface water XAD column and filter samples are discussed below. PCB homologs are described in Appendix D1.5, Section D1.5.2.1. Stacked bar graphs depicting the PCB homolog distributions in the surface water dissolved (XAD column) and particulate (XAD filter) samples by flow condition and river mile are presented in Figures D3.3-1 and D3.3-2. Station location labels and flow conditions are provided on the x-axis, and river mile is indicated on the secondary x-axis along the top of the chart. In this data presentation, non-detected (U-qualified) data were assigned a value of zero; therefore, they do not appear on the bar charts. The discussion of patterns and trends in the PCB homologs is qualitative based on visual examinations of the stacked bar graphs.<sup>2</sup>

The PCB composition of the particulate fraction generally exhibited a more highly chlorinated pattern than the PCBs in the dissolved phase. Several November 2006 stormwater-influenced samples, which exhibited greater contributions from monochlorobiphenyls (monoCBs) and/or dichlorobiphenyls (diCBs) than other particulate samples and their dissolved counterparts, were exceptions to this pattern. This PCB distribution reflects the greater solubility and lower partitioning coefficients of the less-chlorinated congeners, as described in Section 6 of the RI report.

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<sup>1</sup> DDX represents the sum of the 2,4'- and 4,4'- isomers of dichloro-diphenyl-dichloroethane (DDD), dichloro-diphenyl-dichloroethene (DDE), and dichloro-diphenyl-trichloroethane (DDT).

<sup>2</sup> It is important to note that patterns apparent in the stacked bar charts should be interpreted with caution. Changes in chemical composition and apparent trends shown by the bar charts may be indicative of significant patterns (e.g., distinctive source contributions), or they may be within the range of normal data variability. Source identification and allocation are complex multivariate problems. The pattern shifts discussed here based on stacked bar chart presentations may be suggestive, but cannot be interpreted directly as or attributed to localized sources. Such a characterization would require rigorous quantitative forensic analysis, which is outside the scope of this RI/FS.

The PCB composition was generally similar in the dissolved fractions of the four Study Area transect locations and the downstream transect (Station W027, Multnomah Channel) during all sampling events. The dissolved PCBs at the transect locations generally consisted of a fairly equal mixture of diCBs, trichlorobiphenyls (triCBs), tetrachlorobiphenyls (tetraCBs), and pentachlorobiphenyls (pentaCBs), with contributions from hexachlorobiphenyls (hexaCBs). The sample from transect W005 (RM 4) collected during the January 2006 high-flow event had a high percentage of tetraCBs and no diCBs. However, this sample had a relatively low total PCB congener concentration (73 pg/L) and, therefore, this homolog distribution may be reflective of this low concentration.

Generally, the PCB compositions in the dissolved fraction of the upstream transect (W024, RM 16) exhibited a less chlorinated pattern than the PCBs in the Study Area transect samples. The samples from the low-flow events collected at Station W024 had high proportions of diCBs. Conversely, the sample from this station collected during the January 2007 high-flow event was characterized by a high proportion of monoCBs. The PCB homolog patterns in stormwater-influenced samples collected from W024 were similar to stormwater-influenced samples from the Study Area.

The more highly chlorinated PCB composition of the particulate fractions of the transect locations is reflected in the predominance of tetraCBs, pentaCBs, hexaCBs, and heptachlorobiphenyls (heptaCBs), with spatial variations in the proportions of each homolog present. The PCBs at transects W023 (RM 11) in November 2004 (low-flow), from W023E in September 2006, and the near-bottom (NB) sample from W005 (RM 4) in January 2007 (high-flow) contained higher proportions of hexaCBs and heptaCBs than samples collected during other events. The sample from transect W025E (RM 2) collected during the November 2006 stormwater-influenced event contained a higher proportion of triCBs than samples from other events. The W023 (RM 11) sample collected during the November 2004 low-flow event may have been influenced by stormwater discharges from a nearby outfall (OF-45) due to a relatively heavy rainfall event (0.37 inch) on the day the sample was collected (Integral 2006); however, the September 2006 low-flow sample from the east side of this transect had a higher total PCBs concentration and a similar PCB composition to the November 2004 sample. No stormwater discharges were noted during the collection of the September 2006 sample. The interpretation of these surface water samples may be confounded by maintenance dredging conducted at Glacier's docking facility located at RM 11.3. Glacier apparently conducted dredging following approval in June 2004 by the U.S. Army Corps of Engineers. Attempts to obtain post-dredging information have not been successful.

The PCB composition of particulate fractions of the upstream transect station W024 (RM 16) generally exhibited a less chlorinated pattern than the PCBs in the Study Area transect samples upstream of RM 2 for the low- and high-flow sampling events. The stormwater-influenced (September 2006) NB sample at this station had a similar PCB composition to the Study Area transect profiles, while the near-surface (NS) transect

from this event exhibited the same less-chlorinated pattern observed at this station during the other sampling events.

The particulate fractions of the Multnomah Channel transect, station W027, exhibited PCB profiles similar to that of the Study Area transect stations during the high- and low-flow sampling events. The PCB profile at station W027 during the September 2006 stormwater-influenced event was similar to the profiles of the west and mid-channel samples from transect W025 (RM 2) collected during the same event, exhibiting a more highly chlorinated PCB profile. The east sample from transect W025 exhibited a less chlorinated PCB profile than other transect stations during the stormwater-influenced event. PCB patterns in several other samples from location W025 were also less chlorinated than other Study Area transect samples.

Several of the single-point particulate fraction samples from the November 2006 stormwater-influenced sampling contained unusually high proportions of the less chlorinated homolog groups in comparison to the other sampling events. At station W037 (RM 9.6, west bank), the NB sample had a higher proportion of diCBs and the NS sample had higher proportions of monoCBs and diCBs. Similarly, the station W038 (RM 9.9, east bank) NB sample had higher proportions of monoCBs and diCBs. Higher proportions of monoCBs and diCBs were observed in the NS sample at station W031 (RM 6.1) and in the NB sample at station W028 (RM 3.6). The dissolved fractions of these samples had a similar homolog distribution to the other samples from these locations. MonoCBs accounted for 91 percent of PCBs in the dissolved fraction of the NS sample at station W030 (RM 5.5). This sample had a high total PCB congener concentration (2,370 J pg/L). With the exception of station W037 (RM 9.6), the corresponding NS or NB samples did not exhibit similar distributions. These findings would point to a stormwater-related source of monoCBs and diCBs near these locations.

The PCB homolog composition in samples from the NS and NB locations differed from that of the transect samples to varying degrees, likely reflecting local sediment conditions or upland sources. With the exceptions mentioned above, the NS and NB samples exhibited similar PCB distributions at both the NB/NS transect and single-point stations. The PCBs in Swan Island Lagoon, stations W018 (RM 8.3) and W035 (RM 8.5), were slightly more chlorinated overall than PCBs in the transect samples and the sampling locations in the main river channel, with the exception of particulate fractions from Willamette Cove (station W013, RM 6.7) and station W029 (RM 4.4), both of which are discussed below. The predominant homolog groups in this area are pentaCBs, hexaCB, and heptaCBs.

At station W015 (RM 6.9) on the west bank, the abundance of tetraCBs was generally slightly less than at station W016, located less than half a mile upstream. However, in November 2004, the triCBs were unusually abundant at this station in both the particulate and dissolved fractions. The total PCB congener concentration in the November 2004 sample was also unusually high (1,290 pg/L in the particulate fraction and 639 J pg/L in the dissolved fraction). The PCB concentration and homolog profiles

imply contributions from an additional source or sources in November 2004. Because rainfall of 0.24 inch was recorded on this sampling date (Integral 2006), a source or sources related to stormwater discharge near this sampling location is possible.

In Willamette Cove, station W013 (RM 6.7) east bank, the total PCB concentration was high relative to other areas (maximum of 9,560 J pg/L for particulate PCBs and 2,420 J pg/L for dissolved PCBs). The PCB profile in the particulate fraction was more chlorinated than other areas, dominated by hexaCBs and heptaCBs. The dissolved PCB profile was similar to that of the transect samples.

### **D3.3.3 Patterns and Trends of PCDD/Fs in Surface Water**

Stacked bar graphs depicting the PCDD/F homolog distributions in the surface water dissolved (XAD column) and particulate (XAD filter) samples by flow condition and river mile are presented in Figures D3.3-3 and D3.3-4. The discussion of patterns and trends in the PCDD/F homologs is qualitative based on visual examinations of the stacked bar graphs.

Overall, the PCDD/F homolog profiles were dominated by octachlorodibenzo-p-dioxin (OCDD) and heptachlorodibenzo-p-dioxins (HpCDDs) in both the dissolved and particulate fractions. At most transect stations and in most sampling events, OCDD constituted more than half of the PCDD/Fs in the particulate fraction, and from 30 to 95 percent of the PCDD/Fs in the dissolved fraction. HpCDDs accounted for another 15 to 30 percent of the total in both the dissolved and particulate fractions. As would be expected, the dissolved fraction generally contained a greater abundance of the less chlorinated homolog groups than the particulate fraction. The homolog pattern for the particulate fraction PCDD/Fs varied little from transect to transect and from upstream to downstream of the Study Area.

In the dissolved fraction of the transect samples, only a few samples differed from the trend of OCDD and HpCDD dominance. The NS sample from the eastern bank at transect W024 (RM 16) and the eastern bank sample from transect W025 (RM 2) from the January 2007 sampling event, and the November 2006 sample from the west bank at transect W025 exhibited high abundance of tetrachlorodibenzo-p-dioxins (TCDDs). Two samples from the November 2006 sampling event had very low (<0.01 pg/L) total PCDD/Fs concentrations, and only TCDDs were detected in these samples. With these exceptions, only minor differences between the transects were observed; the low-flow sampling events exhibited higher proportions of the less chlorinated homolog groups in the dissolved fraction, and the upriver stations exhibited a less chlorinated profile than those in the Study Area.

The NS and NB transects had very similar particulate PCDD/F homolog profiles during all sampling events, with similar dissolved profiles during low-flow events. Homolog patterns in the NS samples were different than their corresponding NB samples at stations W011 (RM 6.3) and W005 (RM 4) in the November 2006 stormwater-influenced sampling event and at station W024 (RM 16) in the January 2007 high-flow

sampling event. The NS and NB single-point samples also generally exhibited similar particulate and dissolved PCDD/F homolog profiles during all events.

The single-point samples from stations W035 (RM 8.5) and W033 (RM 7) exhibited similar PCDD/F homolog profiles to the transect stations in both the dissolved and particulate fractions under high-flow and stormwater-influenced conditions. These stations were not sampled under low-flow conditions.

However, at Station W015, on the western riverbank at RM 6.9, furans were somewhat more abundant than at other locations during all sampling events, in both the dissolved and particulate fractions. The pattern of the dioxins was similar to that of the transect locations. This area may be influenced by a different PCDD/F source compared to the river as a whole.

In Willamette Cove, stations W013 and W032 (both at RM 6.7), the profile for PCDD/Fs in the dissolved and particulate fractions generally resembled the profiles at the transect locations during each sampling event, but the particulate PCDD/F concentrations found at this location were consistently higher than at nearby transect station W011 (RM 6.3). The PCDD/F patterns in field replicate samples LW2-W3013-2 F (particulate phase, July 2005) and LW2-W2013-2 C (dissolved phase, March 2005) included a distinctly larger fraction of dioxins and a smaller furan fraction than the respective “parent” samples and were not similar to transect Station W011. These replicate samples were collected sequentially, a day apart, and may reflect temporal differences in the PCDD/Fs in Willamette Cove.

#### **D3.3.4 Patterns and Trends of DDx in Surface Water**

Stacked bar graphs depicting the DDx patterns for the surface water dissolved (XAD column) and particulate (XAD filter) samplings by flow condition and river mile are presented in Figures D3.3-5 and D3.3-6. The discussion of patterns and trends in the DDx distributions is qualitative based on visual examinations of the stacked bar graphs.

The DDx distributions for the dissolved fractions varied little from transect to transect within each sampling event, including the stations upstream and downstream of the Study Area. Patterns differed between flow conditions, however. The high-flow transect samples were dominated by the 4,4'-isomers of DDE and DDT, with generally decreasing contributions from DDT as the transects move downriver. The low-flow and stormwater-influenced transect samples had much higher proportions of DDD, primarily the 4,4'-isomer, with a substantial contribution by 2,4'-DDD. For the transects, the contribution of 4,4'-DDD varied with sampling event, whereas the contribution of 2,4'-DDD increased overall moving downriver.

Patterns for particulate DDx were similar to dissolved DDx for high-flow transects, dominated by the 4,4'-isomers of DDE and DDT. The proportion of 4,4'-DDT was more consistent upstream to downstream in the particulate fraction than in the dissolved fraction. 2,4'- and 4,4'-DDD dominated the particulate DDx under low-flow conditions



at most transects, with generally decreasing contributions from 4,4'-DDT and increasing contributions from 2,4'-DDD as the transects move downriver. The March and July 2005 transect samples at stations W023 (RM 11) and W005 (RM 4) had higher fractions of 4,4'-DDE than other transect samples, while the 4,4'-DDE contribution in the dissolved fractions of these samples was similar to other transects. The particulate DDx patterns for the transect samples taken during stormwater-influenced flow conditions were also generally dominated by the DDD isomers, although 4,4'-DDE and 4,4'-DDT were also prevalent in these samples. The DDD isomers were not detected in stormwater-influenced samples from the upriver transects (W023 and W024), or from the downriver transect at RM 2 (W025) east bank sample. The total DDx concentrations at RM 16 and RM 2 transects were low during the stormwater-influenced event relative to other transects.

The NS and NB samples were generally similar in most flow conditions for both dissolved and particulate DDx in both transect and single-point samples. Patterns for the NB and NS samples were different at station W011 (RM 6.3; November 2006 stormwater-influenced sampling event), station W031 (RM 6.1; January 2007 high-flow sampling event), and for station W024 (RM 16; November 2006 stormwater-influenced sampling event), where the patterns may be obscured by method sensitivity limits.

The DDx compound distribution for the dissolved and particulate fractions of the single-point stations were generally similar to those of the transects in high-flow conditions, with the exception of particulate DDx in the NB sample and dissolved DDx in both samples for location W031 (RM 6.1). The particulate W031 NB sample shows higher fractions of the DDD isomers and less 4,4'-DDT than the paired NS sample and the other single-point or transect stations.

During low-flow conditions, stations W016 (RM 7.2) and W015 (RM 6.9) total DDx concentrations were much higher than the other samples (5 to 60 times higher in the dissolved fraction and 14 to 80 times higher in the particulate fraction). These stations are both on the west bank of the river, located a short distance apart (0.3 mile). The particulate DDx patterns varied fairly widely between the two stations and between sampling events at each location, and were distinct from patterns in surrounding areas and at the transect locations at RM 6.3 and 11. Dissolved DDx patterns at these two locations were more consistent and included a larger fraction of DDD than is typical in the Study Area. Under stormwater-influenced conditions, the DDx concentration at nearby station W033 (RM 7) was higher than surrounding areas, but the DDx composition did not vary as distinctly.

### **D3.3.5 Patterns and Trends of PAHs in Surface Water**

Stacked bar graphs depicting the PAH distribution by individual PAHs and summed by number of rings in the surface water dissolved (XAD column) and particulate (XAD filter) samples by flow condition and river mile are presented in Figures D3.3-7 and D3.3-8. A summary of PAHs included in each sum is provided in Appendix D1.5, Table D1.5-1.

The dissolved PAH profiles varied between locations and flow events. During all sampling events, low-molecular-weight polycyclic aromatic hydrocarbons (LPAHs) (i.e., two-ring and three-ring PAHs) accounted for at least 50 percent of the dissolved PAHs at most transect, as well as single-point, stations. The two-ring PAHs (i.e., naphthalene and 2-methylnaphthalene) were dominant in many samples. In several samples, these results were restated as not detected during data validation, as discussed below, confounding the interpretation. The principal three-ring PAHs in many of the samples were acenaphthene and phenanthrene, although fluorene and anthracene were also present in many of the samples. Fluorene was dominant in two stormwater-influenced samples, collected from W023 (RM 11) and W024 (RM 16).

Generally, the remainder of the dissolved PAH profile consisted of four-ring high-molecular-weight polycyclic aromatic hydrocarbons (HPAHs), primarily fluoranthene and pyrene in the high- and low-flow events. With several exceptions, the four-ring PAHs in the November 2006 stormwater-influenced sampling event were chiefly chrysene upstream of RM 8.5 and fluoranthene downstream of this point.

PAH patterns are affected by the presence of elevated detection limits, which result when individual PAHs are restated as not detected in the samples, since non-detects are treated as zeros in the evaluation of PAH patterns. Elevated detection limits may obscure the presence of a PAH at a concentration above the method detection limit. The concentrations reported by the laboratory for each of the PAHs in one or more samples were restated as not detected during data validation. Reasons for restating data as not detected included PAHs detected in laboratory and field blanks and details related to identification of the PAHs (i.e., ion abundance criteria were not met on the mass spectrometer). Data for XAD filter and column samples were affected. Results for LPAHs were restated as not detected more frequently than HPAHs. The evaluation of PAHs in this section takes elevated detection limits into consideration.

The PAH profiles in the particulate fractions also varied between sampling locations and flow events. Among transect locations, the low-flow and stormwater-influenced samples included primarily HPAHs with four and five rings, with fluoranthene, pyrene, and the benzo(a)fluoranthene isomers prevalent but many other HPAHs present as well. Samples from the high-flow sampling events were still predominantly four- and five-ring HPAHs but had more contribution of LPAHs, primarily the three-ring phenanthrene. The six-ring PAHs in the high- and low-flow events consisted of both benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, while the stormwater event consisted almost entirely of benzo(g,h,i)perylene. Particulate PAHs in single-point samples varied from these patterns in many locations, particularly during low-flow conditions.

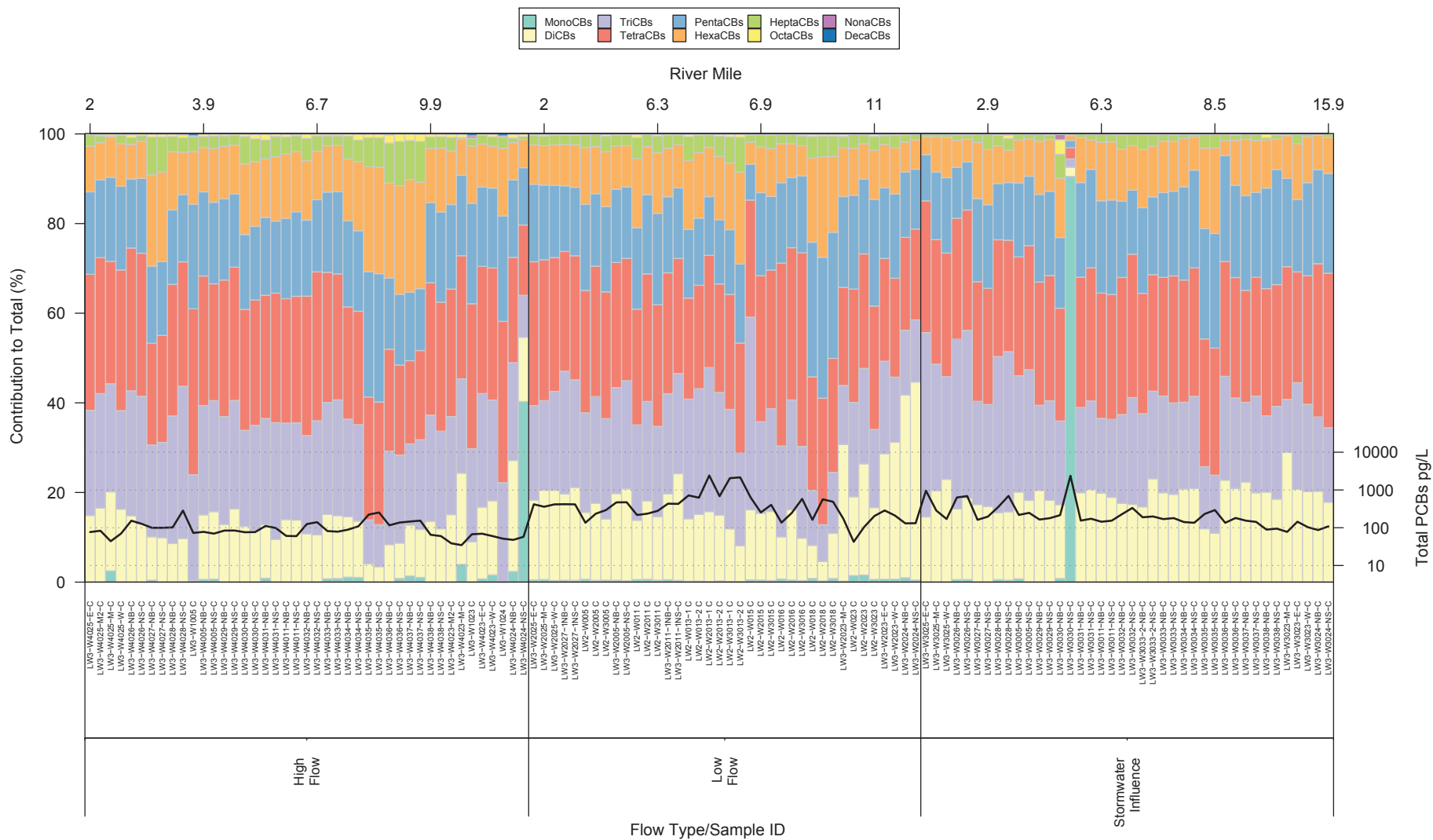
There was generally little difference in composition between the NS and NB samples for both transect and single-point samples. In the November 2006 stormwater-influenced sampling event, the dissolved NS samples at stations W024 (RM 16), W035 (RM 8.5), and W005 (RM 4) all had high contributions from 2-methylnaphthalene (a two-ring PAH) that was not present in the NB samples. The NS samples also had total

dissolved PAH concentrations more than double the NB samples. A similar pattern is not seen in the particulate fractions of these samples. The higher NS concentrations may be related to a hydrocarbon sheen observed during sample collection for the stormwater event that was not thoroughly mixed within the water column, resulting in higher concentrations in the NS samples than the NB samples.

#### **D3.3.6 References**

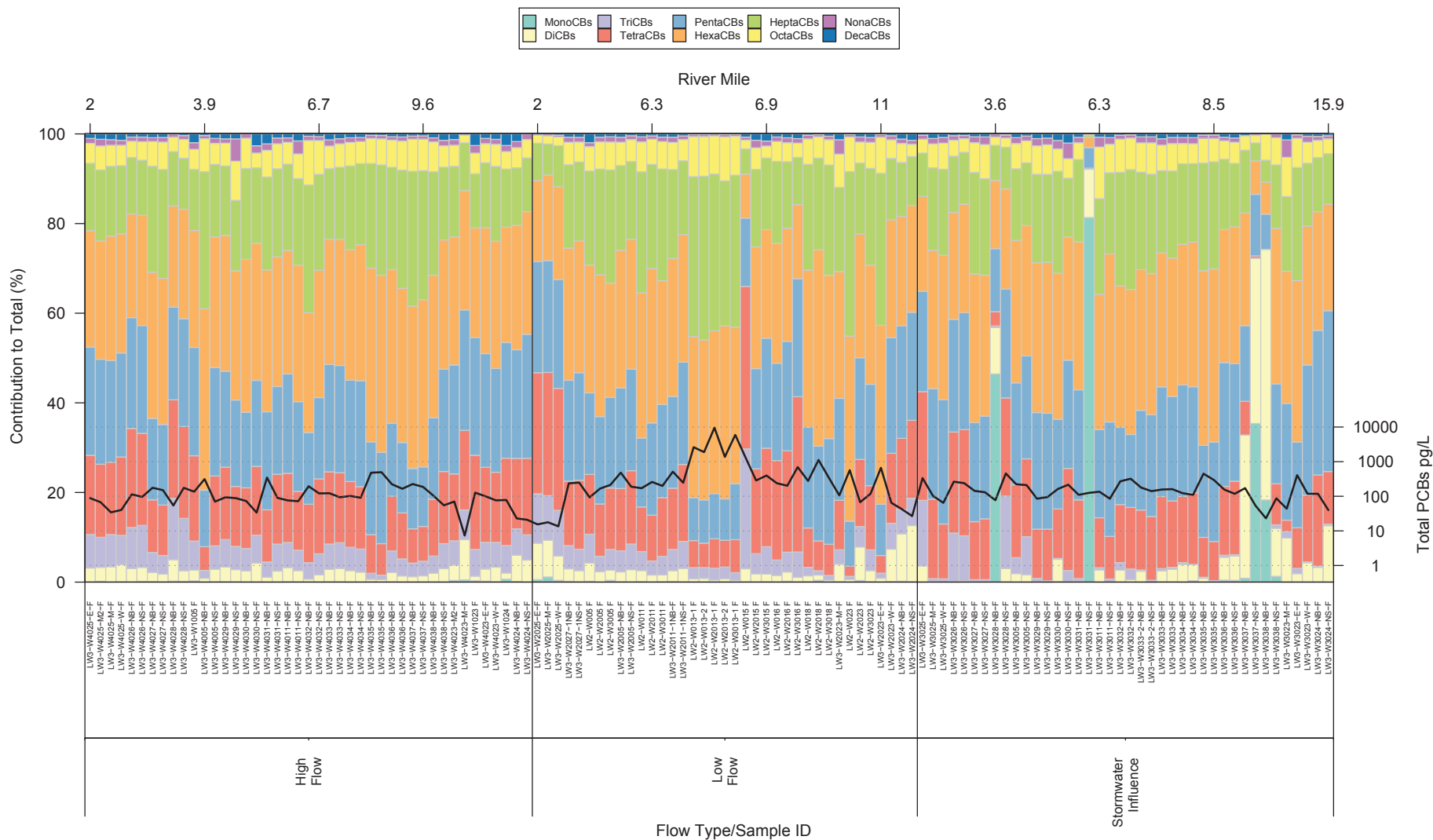
Integral. 2006. Portland Harbor RI/FS Round 2A Surface Water Site Characterization Summary Report. Draft. IC06-0006. Prepared for the Lower Willamette Group, Portland, OR. Integral Consulting Inc., Mercer Island, WA.

## **FIGURES**



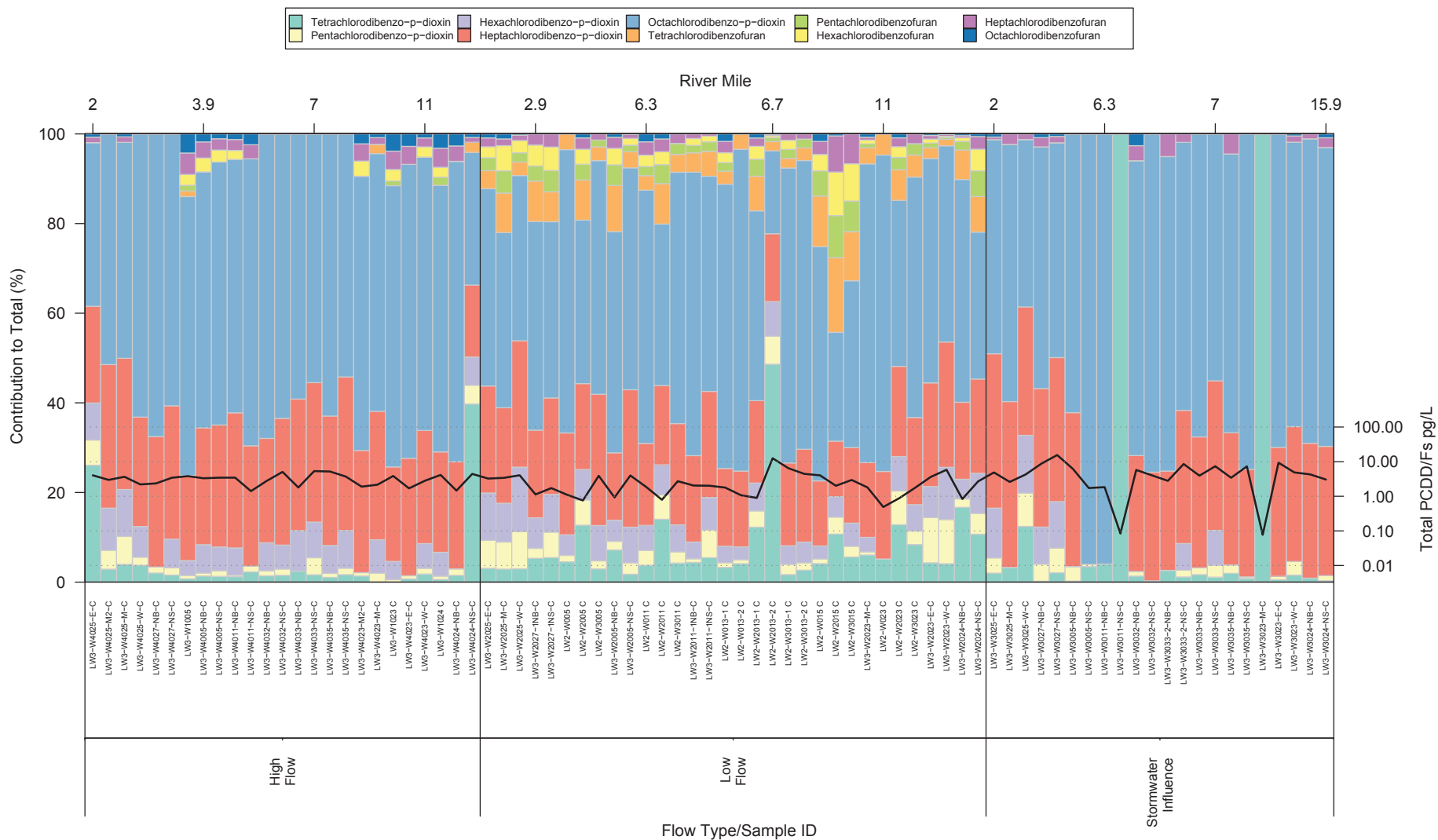
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

**Figure D3.3-1**  
 Portland Harbor RI/FS  
 Remedial Investigation Report  
 Stacked Bar Chart of Dissolved Total PCB Patterns  
 in Surface Water



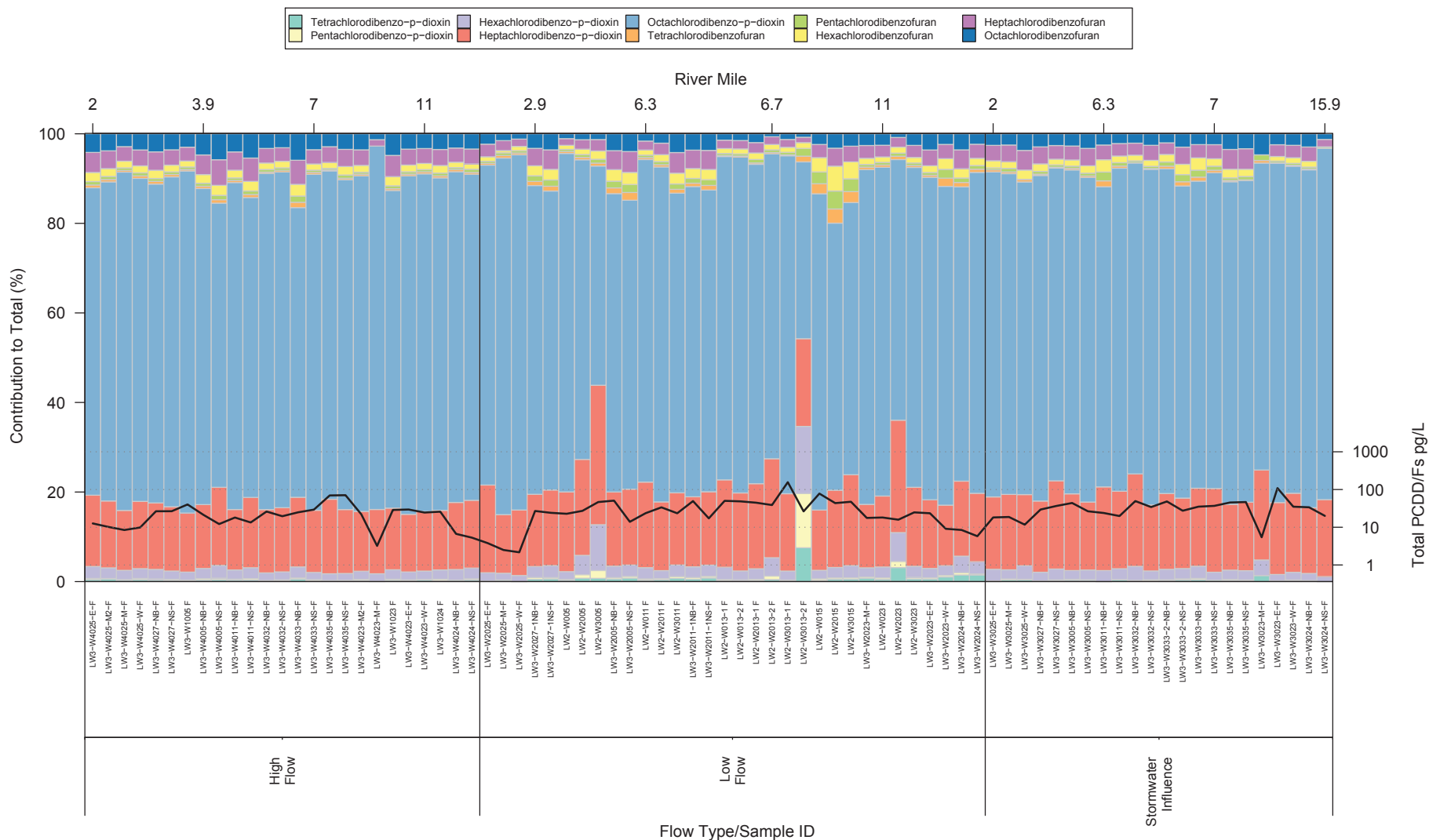
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**Figure D3.3-2**  
 Portland Harbor RI/FS  
 Remedial Investigation Report  
 Stacked Bar Chart of Particulate Total PCB Patterns  
 in Surface Water



Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

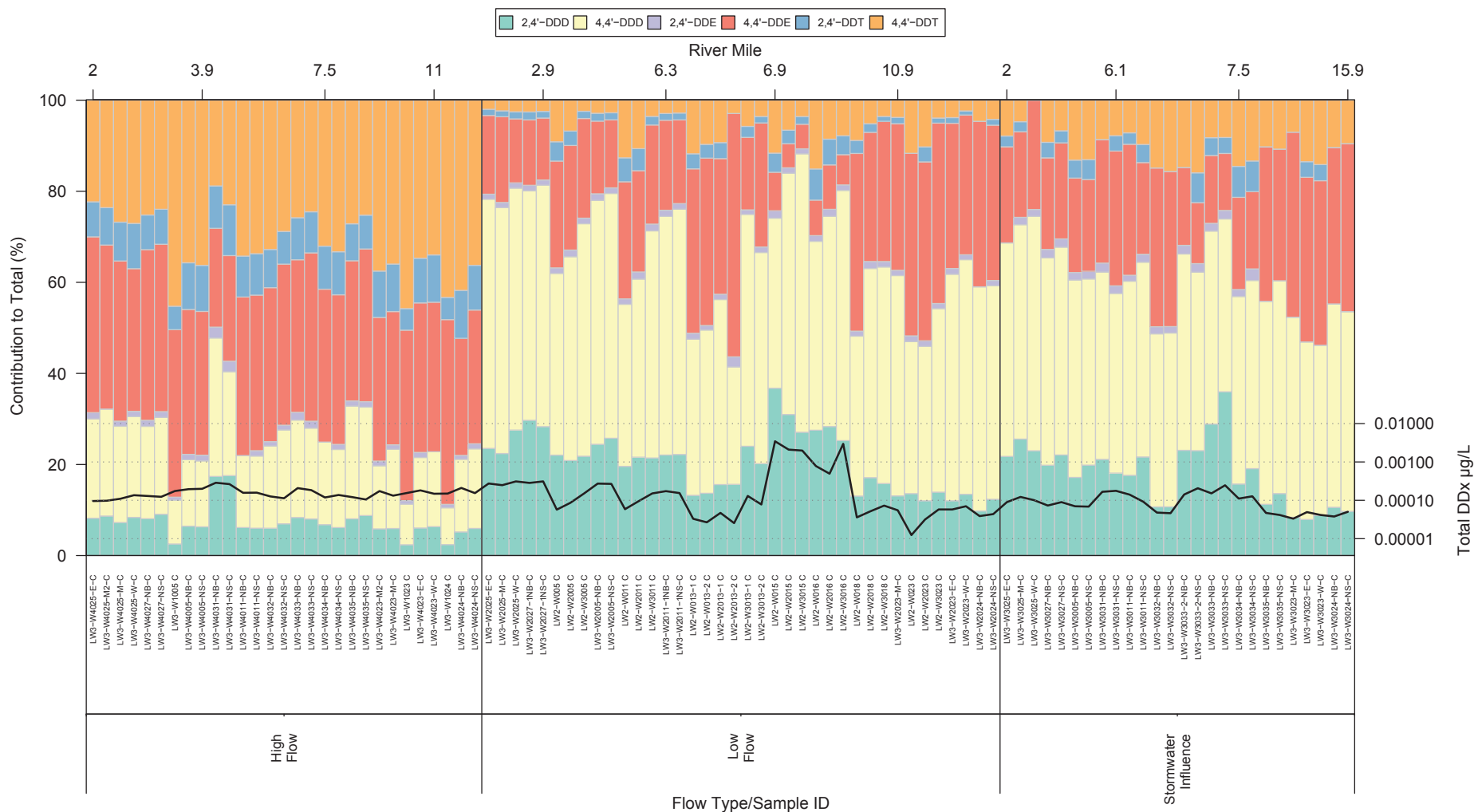
**Figure D3.3-3**  
Portland Harbor RI/FS  
Remedial Investigation Report  
Stacked Bar Chart of Dissolved Total PCDD/F Patterns  
in Surface Water



Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

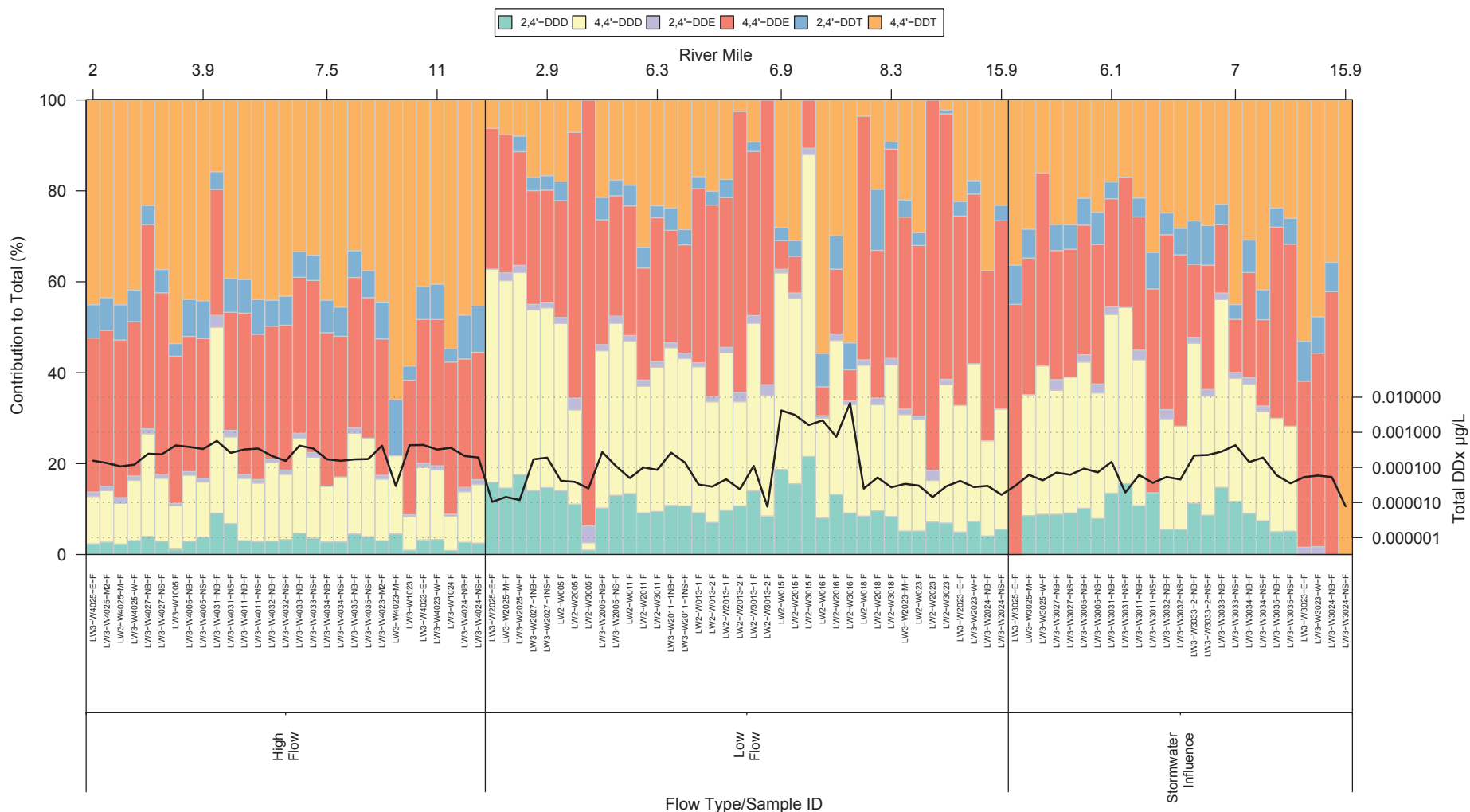
**Figure D3.3-4**  
Portland Harbor RI/FS  
Remedial Investigation Report  
Stacked Bar Chart of Particulate Total PCDD/F Patterns  
in Surface Water





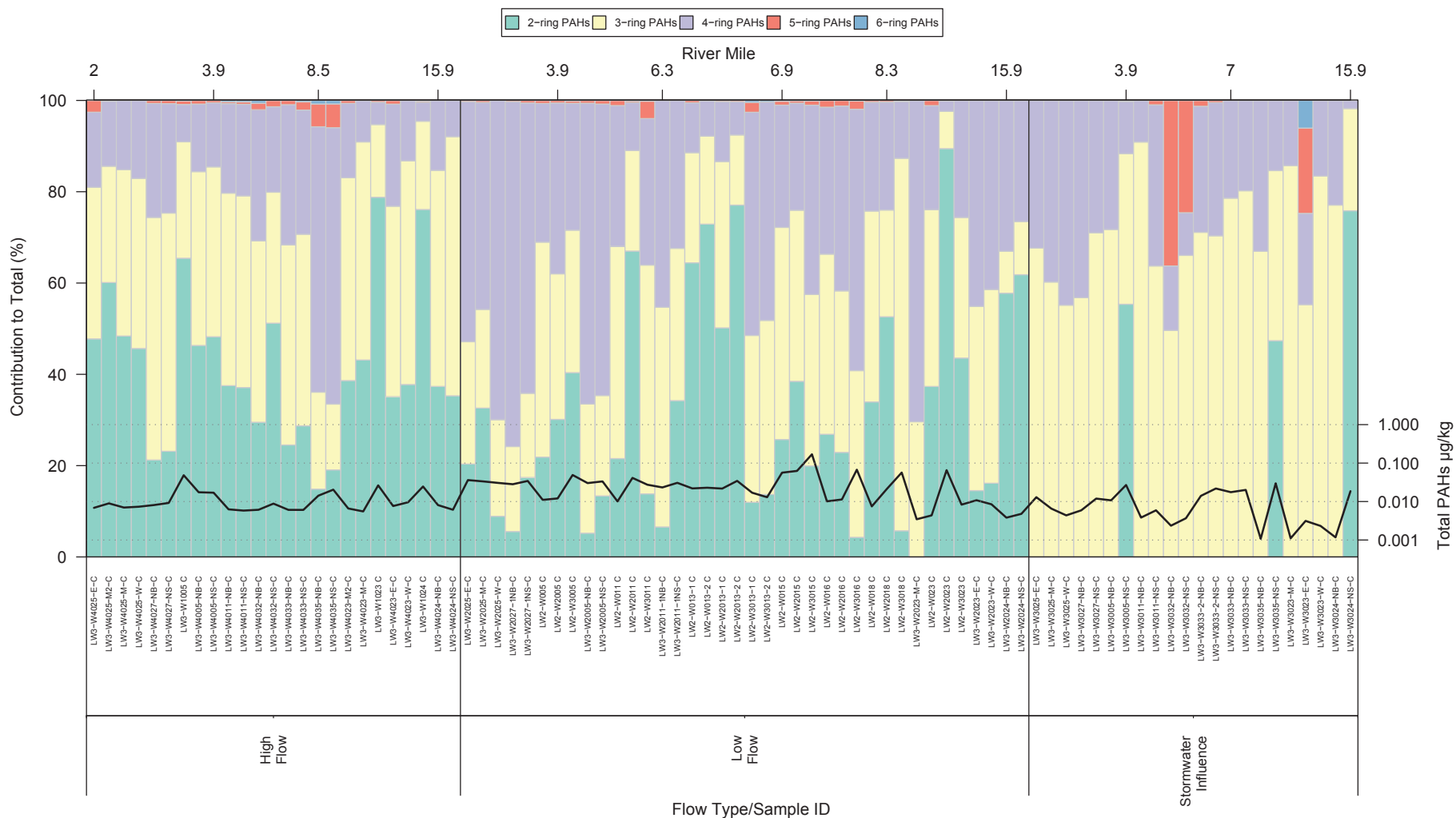
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

**Figure D3.3-5**  
Portland Harbor RI/FS  
Remedial Investigation Report  
Stacked Bar Chart of Dissolved Total DDX Patterns  
in Surface Water



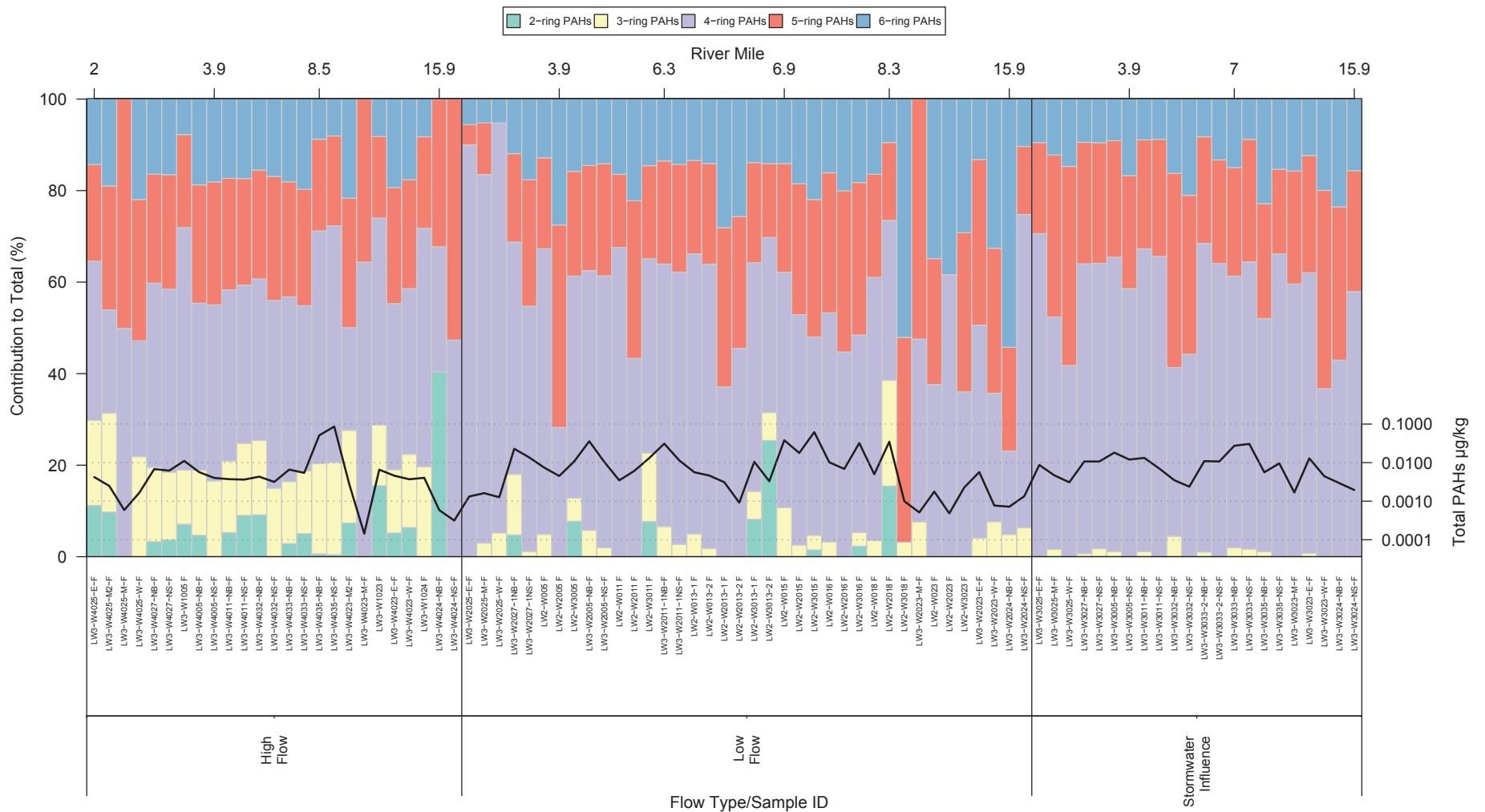
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

**Figure D3.3-6**  
Portland Harbor RI/FS  
Remedial Investigation Report  
Stacked Bar Chart of Particulate Total DDx Patterns  
in Surface Water



Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

**Figure D3.3-7**  
Portland Harbor Report  
Remedial Investigation Report  
Stacked Bar Chart of Dissolved Total PAH Patterns  
in Surface Water



Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

**Figure D3.3-8**  
 Portland Harbor RI/FS  
 Remedial Investigation Report  
 Stacked Bar Chart of Particulate Total PAH Patterns  
 in Surface Water